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Critical Cooling Rates.

EXPERIMENTS have been made by T. G. Digges[1] at the Bureau of Standards, Washington, to determine the "Effect of Carbon on the Critical Cooling Rates of High-purity Iron-Carbon Alloys and Plain Carbon Steels." The high-purity iron was prepared by melting and solidifying electrolytic iron *in vacuo* in crucibles of chemically pure magnesia bonded with a 2–3 per cent. solution of magnesium chloride. The iron contained manganese 0·002, silicon 0·002, nickel 0·007, cobalt 0·007, sulphur 0·004, phosphorus, copper, lead, and magnesium each less than 0·001, oxygen 0·003, nitrogen 0·001, and hydrogen 0·0002 per cent. The ingot, divided longitudinally into two sections, was rolled hot to ¼in. thick and then cold rolled to 0·040in. thick, care being taken to remove all scale before cold rolling. Specimens 0·04in. by 0·275in. by 8in. long were carburised in a mixture of benzene and hydrogen at 1670 deg. to 1700 deg. Fah. (910 deg. to 926 deg. Cent.) in a specially constructed apparatus. After the edges had been ground, the specimens were heated at the same temperature in an evacuated quartz tube to secure uniformity, and cooled in the tube in air. This rate of cooling in all cases gave fine sorbitic pearlite. The times required for carburising fell on a smooth curve in relation to the final uniform carbon content of the specimens, viz., for 0·4 per cent. carbon, 20 min.; for 0·8 per cent., 60 min.; and 1·2 per cent., 160 min. For comparative purposes tests were also made on a steel containing carbon 0·20, manganese 0·46, silicon 0·15, sulphur 0·025, phosphorus 0·043, nickel 0·11 per cent., carburised by heating at 1700 deg. Fah. in an 85 : 15 wood charcoal barium carbonate mixture. The hardenability of a steel depends on the stability of the austenite on cooling through the critical range of temperature. If, by a continuous quenching, austenite is cooled through this temperature range without decomposition, it transforms only at a much lower temperature to martensite, and in this condition the steel is fully hardened. In the work of Digges the critical rate of cooling was taken as the average rate of cooling between 1110 deg. and 930 deg. Fah. (593 deg. to 499 deg. Cent.), which produced in the quenched specimen a structure of martensite with nodular troostite in amounts between 1 and 3 per cent. The specimen used to determine the rate was 0·25in. square and 0·040in. thick. One wire of a chromel-alumel thermocouple was spot-welded to the centre of one face, and the other wire to the centre of the opposite face. The specimens were rapidly heated in nitrogen to the required temperature, held there for 15 minutes and quenched in a bath which sealed the bottom of the vertical tube of the heating furnace. The bath was at atmospheric temperature, and the desired range of cooling rates was obtained by quenching either in oil or in sodium silicate solutions of various concentrations. A photographic time-temperature curve was taken by the aid of a string galvanometer as used by H. J. French and O. Z. Klopsch.[2] The critical cooling velocity was first determined on quenching from a temperature giving constant austenitic grain size with all the carbon in solution in the austenite. In these circumstances the reciprocal of the critical rate of cooling, *i.e.*, the time to cool from 1100 deg. to 930 deg. Fah. bore a linear relation to the carbon contents, viz., for the iron-carbon alloys, 0·1 sec. at 0·30 per cent. of carbon, to 0·28 sec. at 1·2 per cent. of carbon, and for the carbon steels, whether carburised in charcoal-barium carbonate or in benzene-hydrogen, 0·4 sec. at 0·4 per cent. of carbon to 1·04 sec. at 1·2 per cent. of carbon. Thus, the critical rates of cooling were nearly four times as great in the high-purity iron-carbon alloys as in the carbon steels. The slower critical cooling rates, corresponding to deeper hardening, of the carbon steels were mainly due to their manganese content. It was further found that if the carbon steels were quenched from the usually recommended hardening temperatures the critical cooling rate fell to a minimum at about 0·8 per cent. of carbon, then increased rapidly with increase of carbon to about 1·05 per cent. and remained constant with further increase to 1·4 per cent. These critical cooling rates, however, were influenced by variations in austenitic grain size and carbon content of the austenite as well as the total carbon content. H. J. French and O. Z. Klopsch,[3] working with plain carbon steels, and H. Esser, W. Eilender, and E. Spenle,[3] working with high-purity iron-carbon alloys, made from carbonyl iron and carbon, found a decrease in critical cooling rate with increase in carbon content up to about the eutectoid composition, but with further increase in carbon content the critical rates increased again; that is, in high-purity iron-carbon alloys and in plain carbon steel the eutectoid showed a lower critical cooling rate (or deeper hardening) than the alloys with lower or higher carbon. These results were, as Digges points out, influenced by variables other than the carbon content of the materials, viz., in both cases by grain size and in the case of French and Klopsch[2] by the use of quenching temperatures not sufficiently high to ensure complete solution of all the carbon in the highest carbon steel. This last point, it may be added, was specifically dealt with by H. Esser and H. Majert[4] in a paper on the "Influence of Quenching Temperature on the Hardening of Steel." They stated that not only was a quenching temperature above Ac_1 and a definite speed of quenching necessary, but the temperature itself was dependent on the carbon content, pointing out that it is only at a sufficiently high temperature that the

residual ferrite and cementite become dissolved in the austenite. If any of these remain undissolved, they serve on quenching as crystallisation nuclei for the formation of pearlite, and so increase the critical rate of cooling, or tend to reduce depth of hardening. It is well recognised that full depth of hardening can only be obtained when all the carbon has been in solution in the austenite, and it is also well known that the grain boundary is the region in which the breakdown of austenite to troostite begins. Hence the change is less readily suppressed when the grain boundaries are extensive, and thus the critical rate is greater (hardenability less) in fine-grained than in coarsed-grained materials.

In putting forward their explanation Esser and Majert apparently neglected to consider that when ferrite and carbide have been dissolved in the austenite their influence in obstructing grain growth is removed, and that the ensuing grain growth would also tend to decrease the critical cooling rate and so increase hardenability.

It is to this aspect of the questions that the work of Digges directs special attention. It is clear that a constant grain size will have to be secured in specimens intended for the measurements of critical cooling rates, if these are to be strictly comparable.

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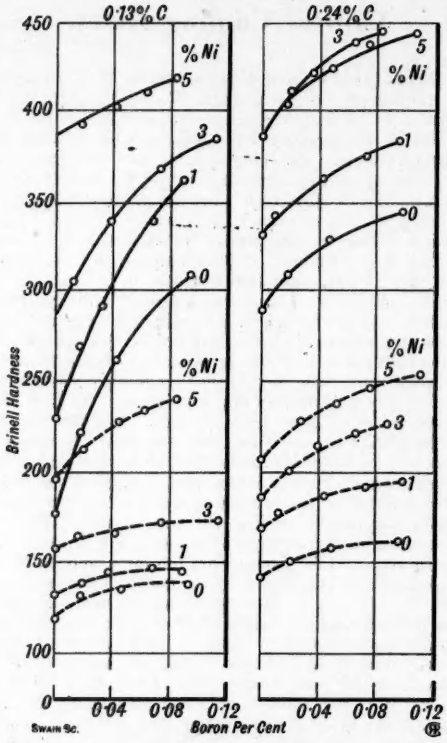
[2] *Trans. Amer. Soc. Steel Treating*, 1924, 6, 251.
[3] *Archiv für das Eisenhüttenwesen*, 1932–33, 6, 389.
[4] *Archiv für das Eisenhüttenwesen*, 1933–34, 7, 319.

The Effect of Boron on Nickel Steels.

FROM time to time claims for the useful properties of boron steels, obtained by "boronising" the surface or by direct alloying, have been put forward. The improvement in properties is usually sought in the direction of increased hardness, but advantages claimed for the surface layer produced by cementation with ferroboron also include considerably increased resistance to acid attack and to oxidation at temperatures up to 800 deg. Cent.

The diagram of F. Wever and A. Müller[1] makes possible some assessment of the probable effect of boron in the light of the constitution of the boron-iron alloys. Up to 8·8 per cent. boron, the boron forms with iron a compound of empirical formula Fe_2B. It is mainly to the presence of this compound that the hardness of boron steel in excess of that of a plain carbon steel of equal carbon content is due. Boron is, however, soluble in γ-iron only to the extent of about 0·15 per cent. at 1174 deg. Cent., and 0·10 per cent. at the A_3 point 915 deg. Cent. In α-iron below A_3 its solubility is 0·15 per cent. The greater solubility of boron in α than in γ-iron makes hardening by retention of a supersaturated solid solution an impossibility. The Brinell hardness number of 311 produced in L. Guillet's steel[2] (carbon 0·22, boron 0·46 per cent.) by quenching was mainly due to its carbon content, the presence of Fe_2B having some slight additional effect. W. Freytag and W. Jenge[3] found that steels alloyed with boron were very hard and brittle, and that the relative effect of the boron was greater in the soft than in the hardened condition. Work carried out in the United States[4] led to the conclusion that boron was harmful on account of the formation of a brittle eutectic which was broken up into hard spherical particles on hot forging. All these early results fall into line with the subsequently determined diagram as also does the fact, determined by Wasmuht[5] that in the almost carbon-free alloys slowly cooled from 930 deg. Cent. the Brinell hardness number rises steadily from about 90 for the pure iron to 350 in the 2·5 per cent. boron alloy, as a result of the increasing amount of Fe_2B present. Wasmuht, with a knowledge of the constitution of the alloys, made a much more systematic study of the subject than his predecessors. Recognising the restricted character of the γ region he endeavoured to achieve the property of hardening



Influence of Boron on the Brinell Hardness of Cast Nickel-boron Steels. Full Lines, Quenched and Tempered (not Above 250 deg. Cent.); Dotted Lines, Normalised.

in these alloys by additions which would extend the γ region. The presence of carbon, of course, has this effect, but Wasmuht avoided its use in order that its hardening effect should not mask the expected hardening due to boron. An addition of 2 per cent. of manganese to the low-carbon boron alloys extended the γ region until the boron-iron-manganese diagram at 2 per cent. manganese showed similar features to the iron-carbon diagram, and the boron alloys on quenching showed Brinell hardness numbers up to 400, and were softened by subsequent tempering. There were signs of an initial rise, indicating some tendency to precipitation hardening, which, however, disappeared quickly at temperatures above 150 deg. Cent. The austenitic chromium-nickel steels showed a diminishing solubility for boron with fall of tempera-

ture and were accordingly subject to precipitation hardening. No increase of hardness resulted from quenching from 1000–1200 deg. Cent., the γ condition remaining unchanged, but marked temper hardening was observed on reheating at 700–800 deg. Cent.

A study of the "Effect of Boron up to 0·1 per Cent. on the Mechanical Properties of Cast Steels Containing 0 to 5 per Cent. of Nickel" has been made by G. Naton and E. Piwowarsky.[6] As basis materials they used two Bessemer steels containing 0·13 and 0·24 per cent. of carbon. From these the boron-nickel steels were prepared in 25 kilo. melts by the addition of pure nickel and 20 per cent. ferroboron, and were cast into 32 mm. diameter or 34 mm. by 17 mm. rectangular bars. These were heated at 40 deg. above the critical range, some being quenched in water and others slowly cooled in the furnace. The quenched steels were tested as quenched and also after from one to thirty-two hours reheating at 50 deg., 150 deg., and 250 deg. Cent. Tensile tests were made on specimens 5 mm. diameter and 25 mm. acting length. Notched-bar tests pieces were 10 mm. by 10 mm. by 55 mm. with a notch 2 mm. diameter and 3 mm. deep. The approximate compositions of the steels were:

C.	Si.	Mn.	S.	P.
0·13	0·5	0·5	0·05	0·09
0·24	0·5	0·6	0·06	0·08

with nickel 0, 1, 3, and 5 per cent., making eight series in all, in each of which the boron was varied from 0 to 0·1 per cent. in steps of about 0·025 per cent. The Ac_3 point was raised about 20 deg. for 0·12 per cent. of boron irrespectively of the nickel and carbon contents. The maximum value of the solubility of boron in α-iron was estimated to be about 0·13 per cent. The results of tests are given in the form of curves which clearly indicate that the relative influence of the boron is very similar in all series. The general effect is shown in the diagram.

In the normalised condition increase of boron is accompanied by increased hardness, yield point, and tensile strength, together with reduced elongation and impact value. The increased strength is more pronounced in the high nickel alloys, while the fall in ductility is proportionately greater in the nickel-free steels which have a higher initial value of elongation and impact figure. The approximate range of properties of the normalised steels is shown in Table I. It will be seen that in the actual size of specimen employed the high nickel alloys display a considerable degree of air hardening.

TABLE I.—*Approximate Properties of the Normalised Nickel-boron Steels.**

Nickel, per cent.	0		1		3		5	
Boron, per cent.	0	0·1	0	0·1	0	0·1	0	0·1
Carbon, 0·13 per cent.:								
Ultimate stress, tons per square inch	27	34	30	36	37	42	44	57
Elongation, per cent.	30	21	17	11	18	12	9	4
Impact figure, mkg. per square centimetre	3·9	1·9	4·2	2·3	3·5	2·2	2·8	1·2
Carbon, 0·24 per cent.:								
Ultimate stress, tons per square inch	33	37	37	39	39	48	49	67
Elongation, per cent.	25	19	24	17	17	10	12	4
Impact figure, mkg. per square centimetre	5·0	2·5	5·8	2·6	4·0	2·4	1·9	1·0

The yield ratio varied from 0·70 to 0·90 as the tensile strength increased.

The range of properties in the steels quenched and tempered at temperatures up to 250 deg. Cent. is indicated by the approximate values given in Table II. In the series of quenched alloys the boron has clearly reinforced the hardenability of the steels, the most pronounced effect being shown in the nickel-free steels in which 0·1 per cent. of boron has practically doubled the tensile strength in the quenched condition. With higher carbon and in the presence of nickel, the initial hardness of the quenched boron-free steels is greater and the proportional change in properties due to the addition of boron not so great.

Reheating the quenched nickel-free 0·1 per cent. boron steel for one hour at 50 deg. Cent. caused an increase in tensile strength of 35 tons per square inch, but in the 5 per cent. nickel steel containing boron the increase was only 4 tons per square inch. After heating all the quenched steels containing boron at 150 deg. Cent. a further slight rise in tensile strength was observed. The boron-free specimens showed no rise in tensile strength on tempering at 50 deg. and 150 deg. Cent. Tempering at 250 deg. Cent. caused

TABLE II.—*Approximate Properties of the Quenched Nickel-boron Steels,* Tempered at Temperatures up to 250 deg. Cent.*

Nickel, per cent.	0		1		3		5	
Boron, per cent.	0	0·1	0	0·1	0	0·1	0	0·1
Carbon, 0·13 per cent.:								
Ultimate stress, tons per square inch	38	70	48	76	57	79	67	83
Elongation	20	8	16	6	14	4	5	3
Impact figure, mkg. per square centimetre	3	1	4	2	2	1	1·5	1
Carbon, 0·24 per cent.:								
Ultimate stress, tons per square inch	44	73	54	83	63	89	73	92
Elongation	18	3	7	3	5	5	5	5
Impact figure, mkg. per square centimetre	3	1·5	2	1	3	2	1·5	1

The yield ratio varied from 0·70 to 0·90 as the tensile strength increased.

* Read from curves in Naton and Piwowarsky's paper.

a fall in tensile strength in all specimens. In all the tempered test pieces a rise in tensile strength was accompanied by a fall in elongation and impact figure. These general indications were confirmed by hardness tests on the quenched steels after one, eight, sixteen, and thirty-two hours' tempering at 50 deg., 150 deg., and 250 deg. Cent. In the 0·1 per cent. boron steels there was an increase in the hardness of the quenched material after tempering at 50 deg. or at 150 deg. Cent. for times up to thirty-two hours; on tempering at 250 deg. Cent. the initial increase was followed by a decrease which brought the hardness below the initial value for the quenched material before the time of tempering reached thirty-two hours. In the boron-free steels tempered at 50 deg. Cent. after quenching, there was either no change or a slight rise of hardness as a result of the first hour's tempering, but this was quickly lost again by tempering for a longer time or at a higher temperature. There appeared, therefore, to be a slight precipitation hardening superposed on the quench hardening in the boron-containing steels. This, however, was small compared with the increased quench hardenability conferred by the presence of boron. It is therefore hardly necessary to follow the author's values for different tempering treatments in great detail. The above notes will indicate whether an upward or downward variation is to be expected from the approximate average values in Table II, as a result of the tempering treatment employed.

It is claimed that the nickel steel alloyed with boron was generally, in spite of its greater hardness, more easily machinable than the corresponding boron-free steel of the series.

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Beryllium and its Alloys.

SOME time ago the publication by W. Hessenbruch of a survey of the properties of beryllium and its alloys was the occasion of a brief summary of information on the subject in the pages of this journal,[1] and a further paper by the same author[2] suggests the desirability of bringing the matter up to date by a similar review, including references to other recent publications on the same subject which are interpolated in the following account of Hessenbruch's paper. One such publication is the paper by C. B. Sawyer and B. R. Kjellgren,[3] contributed to the American Chemical Society's symposium on "Less Familiar Elements," held in Cleveland, Ohio, on December 27th to 29th, 1937. This deals specially with American developments.

Hessenbruch,[2] after mentioning the special difficulties introduced into the electrolytic separation of beryllium by the need of operating at the unusually high temperature of 1400 deg. Cent. (the melting point of beryllium being 1280 deg. Cent.), refers to a recent process[4] in which chloride baths are electrolysed below the melting point of beryllium, yielding spangles of the metal containing 99·0 to 99·5 per cent. beryllium. The metal cannot be used in this form for making alloys unless special precautions are taken against oxidation. It may, however, be remelted in hydrogen or *in vacuo* and compact masses of beryllium (cubes, discs, cylinders, or short tubes) can be prepared. These have a density of 1·86 and a Brinell hardness of 150. They cannot be worked and both on account of their relative brittleness and high price they have no application, except for the use of thin discs as windows in electric vacuum discharge tubes, since their transmission of α and γ rays is very high compared with that of aluminium. Sawyer and Kjellgren name no actual use of metallic beryllium, but call attention to its possible acoustic applications on account of the very great velocity of sound in the metal (more than 2½ times the velocity of sound in steel), dependent on its low density and high modulus of elasticity, viz., 19,000 tons per square inch. This is a calculated figure, but it is confirmed by the fact that the 84 per cent. beryllium-aluminium alloy has a measured modulus of about 16,500 tons per square inch, *i.e.*, about 24 per cent. higher than that of steel. Absence of ductility militates against the use of beryllium-rich alloys. For a sand-cast alloy containing 67·4 per cent. of beryllium and 30·5 per cent. of aluminium which had been suggested for the manufacture of pistons for aircraft engines, Johnson[5] found a Brinell hardness of 75, a maximum stress of 6·2 tons per square inch (probably low on account of premature failure, owing to brittleness), no elongation, and a thermal conductivity about half that of a silicon-aluminium alloy.

The production of ductile beryllium seems to be no nearer to achievement. By distillation of 99·8 per cent. beryllium at 1400 deg. Cent. *in vacuo* in beryllia-lined vessels, Kroll[6] obtained a product of 99·95 per cent. purity, which had a Brinell hardness of 110 and was to some extent malleable when hot, but he concluded that cold brittleness appeared to be a physical property of the element.

With reference to the method of production of the metal referred to by Hessenbruch, it may be stated that electro-deposition of beryllium below its melting point is not new; the work of Sloman and of Fischer and Schwan in this direction was described several years ago.[7] In view of the main use of beryllium the direct production of a copper alloy is probably of more practical interest. Fink and Shen[8] recently described an electrolytic method in which molten copper served as cathode in a fused bath containing beryllium oxyfluoride with sodium and barium fluorides; and Hessenbruch states that the Heraeus-Vacuum-Schmelze A.G. are now able to make beryllium-copper directly by thermal reduction of beryllia in the presence of copper.

BERYLLIUM-COPPER ALLOYS.

By far the greater part of the beryllium obtained to-day goes into copper alloys, the so-called beryllium bronzes. When the beryllium exceeds 1 per cent., they are susceptible to hardening by quenching and reheating. In the quenched condition they may be cold worked, and the subsequent treatment at about 300 deg. Cent. not only removes residual stresses, but also causes precipitation hardening. The properties of these alloys are given in Table I. It is claimed[2] that on account of the strong affinity of beryllium for oxygen, nitrogen, sulphur, and other non-metallic elements, melting these alloys *in vacuo* is of the greatest importance, and examples are given of the excellent ductility of the vacuum-melted alloys. The outstanding use of beryllium bronze is for springs. It possesses advantages over phosphor bronze in having, with a somewhat higher yield point,

TABLE I.—*Properties of Beryllium-Copper Alloys.*[3]

Alloy.	Condition.	Brinell hardness number.	Yield point, tons per sq. inch.	Maximum stress, tons per sq. in.	Elongation, per cent. $l = 10\,d$.	Reduction of area, per cent.	Impact value, mkg. per sq. cm.	Elastic modulus, tons per sq. in.	Electrical conductivity, per cent. of El. Cu.	Coefficient of expansion, 20–200 deg. $\times 10^{-6}$.
Be-Cu	Quenched	65–70	9·5	19·0–22·2	50–55	85–90	13	—	25	—
(α)	Quenched and heat treated	125–130	25·4	28·6–31·7	30–35	80–85	18	6120	28	17·8
1% Be,	Quenched and work hardened	200	45·7	47·6	6	70	15	—	25	—
Sp. gr. 8·6	Quenched, work hardened, and heat treated	230–240	41·3	54·0	12	55	10–12	7000	30	17·7
Be-Cu	Quenched	100–120	17·8	31·7–33·0	60–62	75	15	—	17·5	—
(α)	Quenched and heat treated	330–360	63·5	69·8–76·2	3–4	12·5	1·5	6650	33	16·9
2% Be,	Quenched and work hardened	220	51·4	54·0	6	45	8	—	16·5	—
Sp. gr. 8·3	Quenched, work hardened, and heat treated	365	66·6	79·4	5	15	1·5	7600	25–35	17·1
Be–Cu	Quenched	110–130	21·0	36·2–39·4	30–35	35–40	10–11	7500	17	—
($\alpha+\beta$)	Quenched and heat treated	340–370	66·6	76·2–82·5	3–5	11	1·3	8250	30	17·3
2·4% Be,	Quenched and work hardened	230	57·8	60·3	3	25	3·5	7600	16	—
Sp. gr. 8·2	Quenched, work hardened, and heat treated	375	71·2	85·7	4	45	1·3	8250	20–30	17·2
Co-Be-Cu	Quenched	75–80	9·5	19·0–22·2	30–35	65–80	11	—	27	—
(α), 2·6% Co,	Quenched and heat treated	185–200	31·7	38·1	15–18	35–38	7	7000	38	17·8
0·4% Be,	Quenched and work hardened	150	33·6	34·9	6	50	8	—	24	—
Sp. gr. 8·8	Quenched, work hardened, and heat treated	210	36·8	47·6	15	45	7	7300	40	17·6
Be-Al-Si-Cu	Quenched	170	28·6	47·6	15–20	15–20	2–4	—	9	—
($\alpha+\beta$)	Quenched and heat treated	300	57·2	66·6–73·0	2–3	5–8	1–2	8900	10	18·5
	Quenched and work hardened	220	52·7	54·0–60·3	1–2	8–10	0·5–1	—	8	—
Sp. gr. 8·0	Quenched, work hardened, and heat treated	320	63·5	73·0–79·3	1·5–2·5	10–15	1	8900	9·5	18·1

TABLE III.—*Properties of Beryllium-nickel Alloys.*[2]

Alloy.	Condition.	Brinell hardness number.	Yield point, tons per sq. in.	Maximum stress, tons per sq. in.	Elongation, per cent. on 10 cm.	Impact value, mkg. per sq. cm.	Elastic modulus, tons per sq. in.	Electrical resistivity, microhm-mm.	Coefficient of expansion, 20–200 deg. $\times 10^{-6}$.
Be-Ni,	Quenched	140	22·8	50·8	48	7·1	11,120	0·34	—
2% Be,	Quenched and heat treated	420	50·8	82·5	20	4·0	11,630	0·21	—
Sp. gr. 8·1	Quenched and work hardened	360	95·3	101·6	1·5	4·6	11,430	0·32	—
	Quenched, work hardened, and heat treated	480	95·3	117·5	8	4·5	12,080	0·19	13·9
Be-Ti-Ni,	Quenched	150	25·4	54·0	40	—	—	0·35	—
	Quenched and heat treated	440	50·8	88·9	1·5	—	13,300	0·24	14·9
Sp. gr. 8·1	Quenched and work hardened	360	98·5	104·5	1	—	—	0·36	—
	Quenched, work hardened, and heat treated	500	98·5	120·5	5	—	13,650	0·29	14·8
Beryllium-contracid, *	Quenched	195	26·5	55·9	30	13·9	9,850	1·20	—
	Quenched and heat treated	320	31·5	63·5	23	8·1	10,230	1·23	—
	Quenched and work hardened	350	89·0	95·3	2	3·3	10,730	1·03	—
Sp. gr. 8·3	Quenched, work hardened, and heat treated	450	95·3	117·5	6	2·8	11,760	1·08	13·9

* Contracid is an alloy containing nickel 60, chromium 15, molybdenum 7 per cent., remainder iron.

NOTE.—Much of this information has been available for a long time,[1] but additional data are also given. The Brinell hardness numbers do not always appear to be consistent with the tensile strengths reported.

almost double the fatigue limit in alternating torsion (Table II), and it may be used in circumstances in which the performance of phosphor bronze springs is inadequate, and steel springs are not sufficiently resistant to corrosion. A study of the corrosion of beryllium-copper alloys by Terem,[9] both by loss of weight and by surface examination, showed that their resistance to sea water was good, and that they suffered little attack in dilute hydrochloric and acetic acids. In sulphuric and nitric acids, caustic soda and ammonia, the attack was considerable. In tests carried out in the rotating beam machine, Gough and Sopwith[10] found that there was no diminution in the endurance of beryllium bronze in salt spray. The corrosion fatigue limit, both of phosphor bronze and of beryllium bronze, was as high under these conditions as in air, but phosphor bronze had not so great an endurance limit to start with, viz., 9·8 as against 16·3 tons per square inch. In corrosion fatigue resistance, beryllium bronze was superior to the best stainless steels investigated by them.

The resistance to oxidation of beryllium-copper alloys has also been studied by H. N. Terem[9] in

TABLE II.—*Properties of 4 mm. Diameter Wire for Springs.*[3]

Material.	Yield point in tension.	Torsional fatigue limit.	Modulus of rigidity.
	Tons per square inch.		
Phosphor-bronze, spring hard, unpolished	17·8	±6·3	2860
Beryllium-bronze, 2·5 per cent. Be, quenched, work hardened and treated, unpolished	23·5	±10·8	2860
Ditto, polished	19·0	±12·0	3050

experiments in which alloys containing up to 10 per cent. of beryllium have been heated at temperatures between 610 and 910 deg. Cent. Small quantities of beryllium considerably reduced the rate of oxidation of copper. A minimum rate was reached with 2 per cent of beryllium. This alloy gave the same rate of oxidation as stainless steel at 810 deg. Cent. though at lower temperatures it was oxidised more rapidly than the steel. The behaviour was very dependent on the physical condition of the alloy; powder alloys on account of their fine state of division oxidised rapidly.

In addition to its use for springs, beryllium bronze has a sale as non-sparking safety tools for chemical and explosive factories. It is evident, though not always borne in mind in chemical and oil works, that sparks may be produced by non-sparking tools if the material worked can itself give sparks,[11] Toothed gear wheels are also made of beryllium bronze on account of the high resistance to wear of the hardened alloys; the forged material has a considerably longer life than cast gears. The precipitation which increases the hardness of the alloy simultaneously reduces its electrical resistivity. For this reason certain types of beryllium bronze have proved useful as electrodes in automatic electric welding machines. The properties of one such "conductivity" bronze containing cobalt are shown in Table I.

The binary beryllium-copper alloys will not harden unless the beryllium is at least 1 per cent. There has been a considerable amount of investigation directed towards the development of alloys containing additions, such as cobalt, chromium, and nickel, which render heat treatment effective even when the beryllium content is low. This has led in America to the production of the General Electric Company's "Trodalloy," No. 1, a copper alloy containing 2·6 per cent. of cobalt and 0·4 per cent. of beryllium, and No. 2, with 0·4 per cent. of chromium and 0·1 per cent. of beryllium.

Their properties have been investigated in detail by Harrington,[12] and have also been described by Fuller.[13] No. 1, after water quenching from 900 deg. Cent. and reheating for one hour at 500 deg., has a tensile strength of about 40 tons per square inch, with an elongation of 10 per cent. and an electrical conductivity about 40 per cent. of that of copper. The alloy is said to have good spring properties up to 400 deg. Cent. The No. 2 alloy, quenched from 925 deg. Cent. and reheated to 500 deg. Cent., has a much higher conductivity (73 per cent. of that of copper), but its tensile strength is only a little over half that of alloy No. 1. Alloys of this kind are also being developed in Japan by Sumitomo Metal Industries, Ltd. Inamura and Ohashi[14] have described the properties of "Berychrome No. 1," a copper alloy containing nickel 2, chromium 0·5, and beryllium 0·5 per cent., which is slightly inferior in mechanical properties, but superior in conductivity to ordinary beryllium bronze. In Russia also Amsterdamski[15] has published a series of papers in *Metallurg* on the influence of various additions on the mechanical properties of beryllium-copper alloys. These alloys have also formed the subject matter of several researches[16] dealing with the mechanism of age hardening.

BERYLLIUM-NICKEL ALLOYS.

To return now to the contents of Hessenbruch's paper, the properties of three technical nickel alloys are given in Table III, the binary alloy with about 2 per cent. of nickel, a more complex alloy of nickel with beryllium and titanium, and the alloy of nickel with chromium, molybdenum, iron and beryllium, known as beryllium contracid. All these have good resistance to corrosion, and also to oxidation up to 700 deg. Cent. or 1100 deg. Cent. in the case of beryllium contracid. They may be utilised for high-duty springs, and the durability of a sharp edge or point in the hardened alloys makes them suitable for scalpels, surgical needles and, in the form of seamless tubes, for hypodermic needles. Laissus,[17] in continuation of his numerous experiments on the cementation of metals by various elements, including beryllium, has found that nickel heated in contact with a 3 : 1 mixture by volume of 80 per cent. ferro-beryllium and beryllia for ten hours at 1150 deg. Cent. absorbs beryllium to a depth of 4 mm. (ten times as great a depth as at 1100 deg. Cent.), the Brinell hardness of the surface being increased from 82 to 568 without further treatment after cementation. Though it is claimed that the process is capable of industrial application, no instance is known of the practical use of surfaces cemented with beryllium.

BERYLLIUM-IRON ALLOYS.

At present the binary alloys of iron and beryllium have no technical interest. Though they are susceptible to precipitation hardening they are coarse grained and brittle. In the quenched condition the hardness increases from about 150 to 480 as the beryllium rises from 0·5 to 9 per cent. After reheating it rises from 150 to 700 with increase of beryllium from 0·5 to 5 per cent., and then remains constant. All practical applications of beryllium to ferrous alloys concern the austenitic steels, especially the high nickel steels

of low coefficient of expansion. The application of these alloys for hair-springs dates back several years.[1] The alloy with 36 per cent. of nickel, 1 per cent. of beryllium and the rest iron has a Brinell hardness of 180 as quenched, 360 when hardened, and over 400 when cold work is applied before the final treatment. The coefficient of expansion of the 36 per cent. alloy is increased by the addition of beryllium, but the rise can be minimised by increasing the nickel 38 per cent. As a further possibility, Hessenbruch refers to a beryllium-containing tool steel in which the temper hardening effect of beryllium is superimposed on the quench hardness of carbon steel, but no details are given, as the necessary development work is not yet concluded.

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Corrosion of Steels Containing Tin.

Although tin is not an alloy intentionally added to steel, its existence as a constituent of steel scrap and the consequent occasional occurrence of small quantities of tin in structural steels, make it important to have as full a knowledge as possible of the influence which it can exert on the properties of the steel. The mechanical properties of carbon steels containing small quantities of tin were dealt with by J. H. Whiteley and A. Braithwaite[1] many years ago. They found that 0·06 per cent. of tin seriously impaired the ductility of rail steel, but that in steels of lower carbon content a greater amount might have no detrimental effect. In mild steel the most noticeable effect was a pronounced tendency to red-shortness when the tin exceeded 0·15 per cent. The usual mechanical tests showed that 0·3 per cent. of tin had no detrimental effect on the properties of plates, ½in. or less in thickness, but thicker plates were often decidedly brittle in the bend test when the tin exceeded 0·20 per cent., and a specimen containing 0·17 per cent. of carbon and 0·3 per cent. of tin showed a distinctly lower notched bar impact figure than the corresponding steel free from tin. J. H. Andrew and J. B. Peile[2] investigated mild steels containing up to 0·63 per cent. of tin and found that even the maximum amount did not injure the tensile properties of the steel, though shock resistance was affected when the tin exceeded 0·2 per cent.

The effect of the tin content of steel on its resistance to corrosion has recently been investigated by K. Daeves[3] in a series of atmospheric exposure tests lasting seventy months, in an industrial atmosphere. In addition to a plain carbon steel, steels containing about 0·3 per cent. of tin, 0·25 per cent. of copper, and 0·1 to 0·2 per cent. of phosphorus were exposed in the form of wire. The results are shown in Table I (the actual rate of rusting was somewhat lower than the usual value for an industrial region). The results confirm the conclusion of C. F. Burgess and J. Aston[4] that the addition of 0·3 per cent. of tin to steel has a beneficial effect on its resistance to corrosion. A comparison of steels 3 and 6, which have equal phosphorus content and show almost equal rates of rusting, indicates that the addition of 0·3 per cent. tin to a 0·09 per cent. copper steel has the same effect as raising the copper to 0·27 per cent. without the addition of tin. In steels 2 and 8, with an equal copper content, the same rate of rusting is given by 0·3 per cent. tin as by raising the phosphorus content from 0·015 to 0·125 per cent. In steels 4 and 7, with similar copper content and equal rate of rusting, 0·26 per cent. of tin has the same effect as raising the phosphorus from 0·13 to 0·20 per cent. In steels 2 and 7, with similar copper and phosphorus, the addition of 0·25 per cent. tin with increased carbon reduces the rate of rusting by about 10 per cent. In steels 1 and 6, again with similar, but lower, copper and phosphorus, the addition of 0·29 per cent. of tin (the carbon remaining approximately constant) reduced the rate of rusting by about 16 per cent.[5]

Table I.—*Composition and Corrosion Data.*

Steel No.	C, per cent.	Si, per cent.	Mn, per cent.	P, per cent.	S, per cent.	Cu, per cent.	Sn, per cent.	As, per cent.	Loss by rusting. g./m.² year.	Loss by rusting. mm./year.	Acid attack* cm.³ H_2.
1	0·035	0·05	0·38	0·047	0·030	0·075	—	0·037	578	0·074	46·2
2	0·05	0·194	0·54	0·122	0·036	0·27	—	0·033	422	0·054	56·0
3	0·05	0·005	0·41	0·045	0·036	0·27	—	0·037	485	0·0622	29·8
4	0·13	0·244	0·48	0·202	0·040	0·23	—	0·022	383	0·0491	72·3
5	0·16	0·130	0·41	0·157	0·046	0·27	—	0·030	407	0·0522	47·2
6	0·05	0·006	0·19	0·045	0·046	0·085	0·29	0·033	488	0·0626	18·3
7	0·12	0·006	0·74	0·130	0·048	0·26	0·26	0·033	380	0·0487	44·4
8	0·05	0·006	0·22	0·015	0·046	0·28	0·30	0·030	422	0·054	65·0

* Mean amount of hydrogen evolved in fourteen days' attack in 2 per cent. hydrochloric and sulphuric acids.

Tests of solubility in acid were carried out on specimens in the form of 15 mm. cubes in aqueous solutions containing 2 per cent. hydrochloric and sulphuric acids at 20 deg. Cent. The mean values of

the volume of hydrogen evolved in fourteen days are given in Table I. They show no relationship to the results of the prolonged rusting tests. Steel 4 suffered the greatest attack of acid, but showed, with one exception, the lowest actual rate of rusting in industrial surroundings.

It was found necessary to carry out the rolling of the steels containing tin at a good red heat as they showed a tendency to red-shortness at a dull red heat. No difficulty was experienced in rolling the wire rod to 5 mm. diameter. The tensile properties in this condition, and the results of further cold-drawing tests, are given in Table II.

It is clear from these experiments that the presence of tin will have no deleterious effect on resistance to atmospheric corrosion, but such benefit as it could confer may be better obtained with copper and would be counterbalanced by the tendency to lower ductility and to red-shortness noted by the author in the steels containing tin. This applies equally to steels with and without copper. As noted by R. Bevan,[6] in the discussion of Andrew and Peile's paper, copper-bearing steel with up to 0·5 per cent. of copper and free from tin showed no sign of red-shortness, but steel with 0·25 per cent. of copper and 0·25 per cent. of tin was hopelessly red-short. Thus while information about corrosion resistance is of interest, difficulties associated with segregation, mechanical treatment and cost relative to other effective elements, are sufficient to prohibit the intentional use of tin as an alloy element in structural steel.

TABLE II.—*Tensile Properties and Drawability.*

Steel No.	Yield point.	Ultimate stress.	Elongation ($l=10\,d$).	Reduction of area.	Smallest diameter wire,* mm.	Ultimate stress.	Number of twists.	Number of bends.
	In the rolled condition (5 mm. dia.).					After the last draw.		
	Tons/sq. in.	Tons/sq. in.	Per cent.	Per cent.		Tons/sq. in.	$l=150$ mm.	$r=5$ or 10 mm.
1	20·9	37·0	18	10·5	1·67	66·6	11	7
2	20·3	32·9	25	35·8	1·86	70·5	1	1
3	17·7	29·2	24	28·8	0·70	80·6	67	44
4	19·8	31·8	26	38·9	1·06	83·2	35	19
5	19·9	†	23	31·9	0·80	81·9	57	38
6	19·6	28·9	11	5·5	0·97	78·6	28	19
7	22·0	30·0	—	—	1·20	73·7	19	15
8	18·6	†	18	22·0	2·15	61·0	1	7

* Obtained by drawing the 5 mm. diameter rod without intermediate annealing. † Flaw.

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Thermal Conductivity of Iron and Steel.

EXPERIMENTAL difficulties and the marked effect of variation in the amount of impurity in specimens under test have resulted, until recently, in an unfortunate lack of agreement in the values of the thermal conductivity of iron and steel. A review of earlier results led E. H. Hall[1] in 1900 to recommend as the value for pure iron between 0 deg. and 100 deg. Cent. $0{\cdot}1541(1-0{\cdot}0003\,t)$ cal./cm. sec. deg. Cent. The International Critical Tables (1926) gave 0·148 based on values covering a range 0·136 to 0·160. Determinations made since that date give much higher values for iron of high purity at atmospheric temperature. A value of 0·19 c.g.s. units has been suggested as the best approximation, but there is still considerable lack of agreement with reference both to pure iron and to steels at atmospheric and raised temperatures.

In these circumstances the report of a set of carefully determined values of "The Thermal Conductivity of Technically Pure Iron and some Steels," by H. Esser, W. Eilender, and E. Pütz,[2] is specially welcome. The method they employed is a modification of the Forbes method. In a specially designed apparatus, the details and operation of which are fully described, a series of experiments were made, for each required temperature, on a wire rod specimen 5 mm. or 6 mm. in diameter and nearly 2 m. long, to which were affixed ten thermocouples. First, the rate of cooling of the uniformly heated specimen was determined. Then the temperature gradient along the same bar locally heated at one end was determined. The first experiment gave $\frac{d\,T}{d\,\tau}$ for any temperature, T being the temperature and τ the time. The second gave $\frac{d\,T}{d\,x}$, where x is the distance along the bar. By plotting against one another the values of $\frac{d\,T}{d\,\tau}$ and x, appropriate to the given temperature T_1, T_2, &c., a curve was obtained from which a graphical determination of the area $\int_x^\infty \frac{d\,T}{d\,\tau}\,.\,d\,x$ could be obtained. The flow of heat per unit area of cross section is $\lambda\,.\,\frac{d\,T}{d\,x}$ and also $c\,\rho\int_x^\infty \frac{d\,T}{d\,\tau}\,.\,d\,x$, and by equating these λ can be calculated. In order to obtain the thermal conductivity, it was thus necessary that the specific heat c and the specific gravity ρ at the given temperatures should also be known.

The composition of the steels investigated by Esser, Eilender, and Pütz and the values obtained for the thermal conductivity, together with those of the specific heats and specific gravities used in

calculations are given in Tables I and II. These experimental values are the means of 25–30 measurements.

The values found for electrolytic iron and mild steel No. 1 fully confirm the upward trend of recent determinations. They are considerably higher than the results of E. Maurer[3] and of R. W. Powell,[4] and when extrapolated to room temperature show good agreement with those of A. Eucken and K. Dittrich[5] (0·197 to 0·225 c.g.s. units for electrolytic iron). It seems probable that the removal of the last few 0·01 per cent. of impurities has a very pronounced

TABLE I.—*Composition of Steels Referred to in Table* II.

Steel No.	C, per cent.	Mn, per cent.	Ni, per cent.	Cr, per cent.
1	0·065	0·40	—	—
10	0·29	0·84	—	—
11	0·52	0·63	—	—
12	0·85	0·65	—	—
13	1·10	0·55	—	—
14	1·40	0·53	—	—
15	0·13	0·4	4·5	1·1
16	0·30	0·6	1·5	0·5
17	0·35	0·6	4·5	1·3
21	0·12	—	18·0	27·0
22	1·12	13·5	—	—

effect in improving the thermal conductivity. The steepness of the curves in Fig. 1 as they approach carbon, nil, gives a similar indication, which was also observable in the results of F. Bollenrath and W. Bungardt,[6] and in the work of R. W. Powell. It appears, therefore, that the high values for electrolytic iron, and the considerable fall in value when the carbon becomes appreciable, are entirely justified. The results of different observers at 400–500 deg. Cent. show better agreement.

The effect of carbon content on thermal conductivity is shown in Fig. 1. For each temperature there is fall in conductivity, at first rapid, and then more gradual, as the carbon increases, and for each steel the values decrease with rise in temperature. A fall in conductivity of carbon steels with rise in temperature has been noted by all observers, though that recorded by Donaldson[7] was very slight. The fall is more pronounced over the range 100 deg. to 300 deg. Cent. in the experiments now described than in those of previous workers. The curves of Esser, Eilender, and Pütz show a tendency to cross those of S. M. Shelton and W. H. Swanger,[8] F. Raisch,[9] and E. Maurer at a temperature of about 300 deg. Cent., being higher below, and lower above, that temperature.

Determinations were made of the thermal conductivity of several nickel-chromium constructional steels. It was found, in agreement with previous investigators, that the conductivity is greatly reduced by the alloy addition. Numerically, the values were in good agreement with the occasional determinations previously made on similar steels, and the effect of temperature was similar to that already noted in these steels. As in carbon steels, the conductivity falls, but the fall is slight, thus bringing the actual conductivity at 500 deg. Cent. into closer agreement with that of mild and medium carbon steels.

The austenitic steels have a distinctly lower thermal conductivity than the other classes examined and showed a slight increase in conductivity with

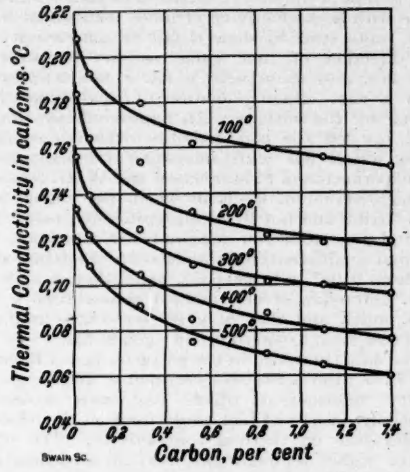

FIG. 1.—*Influence of Carbon Content on the Thermal Conductivity of Plain Carbon Steels at Temperatures from 100 deg. to 500 deg. Cent.*

TABLE II.—*Thermal Conductivity of Iron and Steels.*

Material (for composition see Table I).	Thermal conductivity in cal./cm. sec. deg. Cent. at					Values taken in calculation of thermal conductivity for					
						Specific heat at					Sp. gr.[1] g./cm³.
	100°.	200°.	300°.	400°.	500°.	100°.	200°.	300°.	400°.	500°.	
Electrolytic iron	0·208	0·184	0·157	0·134	0·120	0·114	0·121	0·130	0·141	0·156	7·86
Carbon steel, No. 1	0·193	0·165	0·140	0·123	0·109	0·114	0·121	0·130	0·141	0·156	7·86
" " No. 10	0·180	0·154	0·125	0·105	0·0907	0·116	0·123	0·132	0·143	0·157	7·68
" " No. 11	0·162	0·132	0·109	0·0852	0·0750	0·118	0·124	0·133	0·144	0·158	7·68
" " No. 12	0·160	0·122	0·102	0·0875	0·0695	0·119	0·125	0·133	0·144	0·158	7·68
" " No. 13	0·156	0·119	0·100	0·0800	0·0650	0·120	0·126	0·134	0·144	0·159	7·68
" " No. 14	0·152	0·119	0·0961	0·0760	0·0601	0·121	0·127	0·135	0·145	0·159	7·68
Nickel-chromium steel, No. 15	0·137	0·134	0·130	0·128	0·125	0·094[3]	0·111[3]	0·126[3]	0·144[3]	0·164[3]	7·86
Nickel-chromium steel, No. 16	—	0·073	0·063	0·060	0·058	0·094	0·111	0·126	0·144	0·164	7·86
Nickel-chromium steel, No. 17	0·109	0·101	0·090	0·080	0·071	0·094	0·111	0·126	0·144	0·164	7·86
Austenitic Cr-Ni steel, No. 21	0·049	0·050	0·052	0·053	0·054	0·115[3]	0·119[3]	0·130[3]	0·140[3]	0·160[3]	8·08[3]
Austenitic Mn steel, No. 22	0·0442	0·0448	0·0455	0·0478	—	0·127[4]	0·134[4]	0·140[4]	0·146[4]	—	—

[1] Inserted for all temperatures. [2] According to measurements made in the Technical High School, Aachen. [3] Estimated. [4] According to H. Klinkhardt, Ann. Phys., Lpz., 1927, 84, 167.

rise in temperature. The values were in good agreement with those of other investigators on similar steels, but the increase in conductivity with rise in temperature, though definite, was somewhat less than has sometimes been observed. It is interesting to note that in the steels referred to in Tables I and II those with a conductivity of more than about 0·06 c.g.s. units tend to show a fall in conductivity in the direction of that value as the temperature increases, and those with a lower conductivity to show a rise. No explanation of this tendency is offered by the authors. An approximately similar limit divided the conductivities which rose from those which fell with increasing temperature in the experiments of S. M. Shelton and W. H. Swanger on high-chromium steels in which the change was to a ferritic and not to an austenitic structure. For example, between 100 deg. and 500 deg. Cent. the thermal conductivity of a 5 per cent. chromium steel fell from 0·087 to 0·080 c.g.s. units, that of a 15 per cent. chromium steel remained constant at 0·062 c.g.s. units, and that of a 26 per cent. chromium steel rose from 0·050 to 0·058 c.g.s. units.

The data contained in the paper by Esser, Eilender and Pütz form a valuable addition to the somewhat scanty information which has been available, especially on iron of high purity and on the effect of temperature on thermal conductivity. The effect of the higher temperatures used in hardening and in the usual tempering treatments still, however, awaits investigation.

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Flakes in Steel.

WHETHER or not the "hydrogen theory" is accepted to explain the occurrence of flakes in steel, it will generally be agreed that there are conditions, other than the hydrogen content, which exercise a marked influence on susceptibility to the formation of flakes. A study has been made by E. A. Klausting[1] of some of the conditions present in a series of basic electric steels which showed a high degree of susceptibility to the formation of flakes. The composition of the steels is given in Table I. In order to obtain the highest possible susceptibility to flake formation the ingots were placed in the furnace without preheating, and after 1½ to 3 hours at a temperature of 1180 deg. Cent. were forged into billets 100 mm. square, the forging being completed at 800 deg. Cent. The susceptibility to flake formation was estimated by counting the number of hair cracks in the cross section. Fracture specimens were used as a control, and as a comparison, sections cut from the top, middle, and bottom of the ingot were examined after they had been stored for three days at atmospheric temperature subsequently to an annealing treatment at 800 deg. Cent.

In order to establish the temperature at which the flakes were formed, specimens of the steels 1, 2, 3, and 5 were, after forging, cooled in ashes down to temperatures of 250 deg., 200 deg., 150 deg., 100 deg., 50 deg., 30 deg., and 20 deg. Cent., and were then immediately placed in a furnace at a temperature of 800 deg. Cent. After twenty-four hours the specimens were slowly cooled to room temperature, and then immediately examined for flakes. None was observed in any of the specimens, but after storage at room temperature for a period, flakes were found in a number of the specimens. The author concluded that, apparently, flake formation set in at atmospheric temperature after a period of induction lasting up to thirty hours.

In further experiments the forged specimens were slowly cooled in slag wool down to different temperatures, below which they were further cooled in air. Examination for flakes was carried out three days later. The results showed that a retardation of cooling velocity at the pearlite point, and also immediately above the temperature of the martensite transformation, had a decisive influence on the occurrence of flakes. Their formation was prevented in steels 4 and 6 by slow cooling at a rate of 20 deg. Cent. per hour in the pearlite transformation range, 700 deg. to 500 deg. Cent. In the other steels the slow cooling had to be prolonged at least to 300 deg. Cent., and in the nickel-chromium steels 1 to 3 to 200 deg. Cent. in order to ensure freedom from flakes. In a further series of experiments the forged specimens were immediately placed in a furnace which had a temperature corresponding approximately to that of the pearlite change. After different times they were removed, cooled in air, and three days later examined for flakes. The results of these experiments are summarised in Table II. Flakes were observed unless the steels had been held for a sufficient length of time, viz., six to sixteen hours, depending on the temperature and composition of the steel, for the austenite to pearlite transformation to proceed to completion.

These results were linked up with those obtained in the controlled cooling experiments, by means of a structural study of specimens of steels 1 and 2 in which

TABLE I.—*Composition of the Steels.*

Steel No.	C, per cent.	Si, per cent.	Mn, per cent.	P, per cent.	S, per cent.	Ni, per cent.	Cr, per cent.	Mo, per cent.	W, per cent.
				Max.	Max.				
1	0·10 to 0·16	0·35 max.	0·20 to 0·50	0·03	0·025	2·8 to 3·4	0·55 to 0·90	—	—
2	0·33 to 0·41	0·40 ,,	0·25 to 0·60	0·03	0·03	3·0 to 3·7	1·20 to 1·60	—	—
3	0·20 to 0·30	0·40 ,,	0·25 to 0·50	0·03	0·025	4·0 to 4·7	1·30 to 1·70	—	0·8 to 1·2
4	0·25 to 0·35	0·35 ,,	0·40 to 0·70	0·03	0·03	—	0·80 to 1·20	0·15 to 0·25	—
5	0·95 to 1·10	0·15 to 0·35	0·20 to 0·40	0·027	0·02	—	1·30 to 1·65	—	—
6	1·10 to 1·25	0·35 max.	0·15 to 0·40	0·03	0·03	—	0·10 to 0·30	—	1·8 to 2·2
7	0·90 to 1·05	0·15 to 0·35	0·80 to 1·10	0·03	0·03	—	0·90 to 1·20	—	1·2 to 1·6

the cooling had been started in slag wool and then completed in air. When the structure was free from martensite, flakes were never found. In the other specimens a relationship was observed between the

TABLE II.—*Influence of the Isothermal Pearlite Change on Flake Formation.*

Steel No.	Annealing temperature, deg. Cent.	Time of annealing, hours.	Time beyond which no flakes were found, hours.	Number of flakes in comparable specimens.
1	590 to 620	2, 3, 4, 6, 9, 12, 16, 20, 24	16	35 to 21
2	620 to 640	3, 6, 9, 16, 20, 24	12	57
2	590 to 620	2, 4, 6, 9, 16, 20, 24 ...	9	4 to 40
4	660 to 690	2, 3, 6, 9, 12, 16, 24 ...	6	30 to 57
4	660 to 690	3, 6, 9, 12, 16, 24	6	35 to 86
5	660 to 690	3, 6, 9, 12, 16, 24	9	117 to 120
5	660 to 690	3, 6, 9, 12, 16, 24	9	80 to 100
6	660 to 690	3, 6, 9, 12, 16, 24	9	140
7	660 to 690	3, 6, 9, 12, 16, 24	6	90
7	660 to 690	3, 6, 9, 12, 16, 24	6	140 to 160

number of flakes occurring and the extent of the martensitic regions present in the section.

In summing up the results of this work, the author, while agreeing that the presence of a supersaturated solution of hydrogen is a necessary assumption, maintained that it is not sufficient to account for the formation of flakes. A second condition, also not in itself sufficient to lead to flake formation, was the occurrence in the steel of the austenite-martensite transformation, with the formation of tetragonal martensite leading to a state of high stress in the macrostructure. The formation of flakes does not occur, according to the author, simultaneously with the production of this condition of stress, but follows after storage at room temperature. This apparent induction period he explains as being due to the slow rate of diffusion of hydrogen in steel, though it does not seem clear why the progress of diffusion by which pressures are being reduced should enhance the danger of cracking.

In another paper Klausting[2] discusses the extent to which the measures he advocates to reduce susceptibility to flakes will secure their complete avoidance. Specimens of steel 3 were forged and cooled in slag wool to 250 deg. Cent. in about fifty hours, then treated in the manner described in Table III, and examined for flakes in the usual way. By the slow cooling in slag wool the formation of martensite was avoided; the specimen was cooled in air from 250 deg. Cent., reheated to below Ac_1, and cooled again without suffering any damage.

TABLE III.—*Susceptibility to Flake Formation of Steel* 3 (*Table I*). *After Different Treatments. Intial Treatment; Cooled from Forging Temperature in Slag Wool to* 250 *deg. Cent. in* 50 *Hours.*

Treatment after removal from slag wool at 250 deg. Cent.	No. of flakes.	
Cooled in air and after several days tempered at 640 deg. Cent.	—	—
Immediately normalised from 950 deg., and after three days, tempered at 640 deg. Cent.	42	72
Cooled in air, after twenty-four hours normalised from 950 deg. Cent., after three days soft annealed, tempered at 640 deg. Cent.	60	60

When, however, it was reheated above the critical range, without subsequent precautions in cooling, flakes were found. This was explained by the assumption that the specimen after the first treatment still contained so much hydrogen that it remained susceptible to the formation of flakes. In a specimen from an ingot of another melt, none of the three treatments described in Table III produced any flakes. This difference the author assumed to have been due to different initial hydrogen content of the two materials, the cooling time of fifty hours in slag wool being sufficient for its removal in one case and not in the other. The recommended treatment, directed towards the avoidance of martensite, is thus regarded by the author as a method of inhibiting the production of flakes rather than necessarily eliminating susceptibility to flake formation.

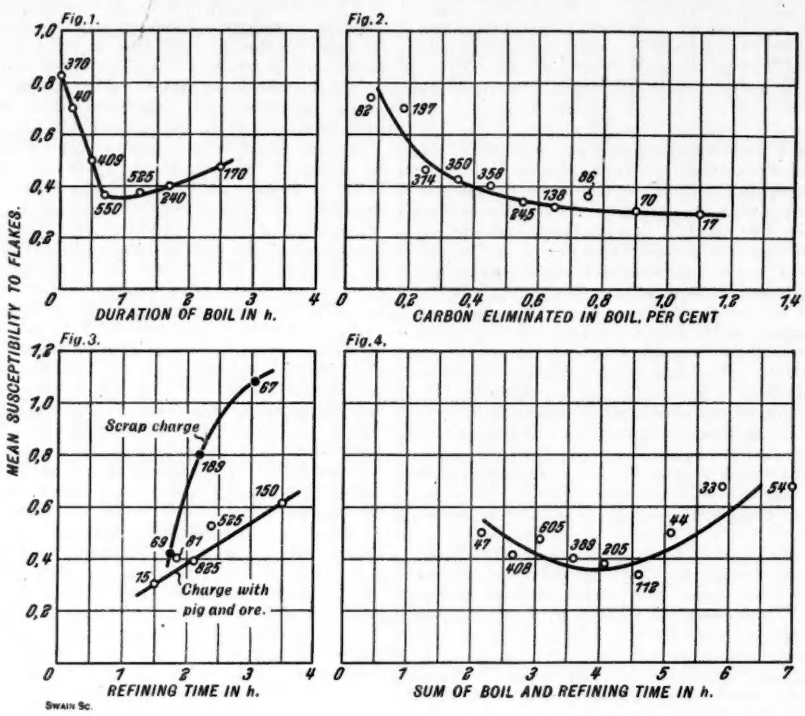
If the presence of hydrogen is regarded as the chief cause, or even a contributory cause, of the formation of flakes in steel, it follows that modifications in steel melting practice which affect the possibilities of hydrogen absorption by the molten metal must exercise a pronounced influence on the susceptibility to flake formation. Interest is therefore attached to the study by A. F. Myrzymow[3] of the tendency to the formation of flakes exhibited by 2000 melts of ball bearing steel. The steels contained carbon 0·95 to 1·1, and chromium either 0·75 to 1·05 or 1·30 to 1·65 per cent., together with other elements as follows:—Silicon, 0·15 to 0·35; manganese, 0·20 to 0·40; sulphur, under 0·02; phosphorus under 0·027; and nickel, 0·2 per cent. The steels were made in basic electric furnaces of 8 and 15 tons capacity, mostly with additions of solid pig iron and ore, but about 20 per cent. of the melts were made from scrap only. The steel was cast into ingots of 1 to 2·3 and occasionally 2·7 tons weight.

To determine the susceptibility of the steel to the formation of flakes, a bar 85 mm. square was rolled from each melt, and from it six specimens were cut and tested for flakes. A number, between 0 and 6, was assigned to the melt in accordance with the number of specimens showing flakes. Thus, in a steel numbered 0 no specimens showed flakes, in one numbered 6 there were flakes in all the specimens. These numbers enabled the mean susceptibility to flake formation of various groups of steel, classified to show the effect of some particular variable, to be calculated, *i.e.*, mean susceptibility=sum of "merit number" for every steel in the group, divided by the total number of steels on the group. In Figs. 1 to 4 the effect of certain variables on mean susceptibility is recorded. It may be noted that at least one of the six specimens showed flakes in 26·2 per cent. of the steels remelted from scrap, and in a smaller number, viz., 18·6 per cent., of those made from charges containing pig iron. Fig. 1 indicates the relation between flake formation and length of "boil," showing that the lowest tendency was reached with a boil of fifty to sixty minutes. Longer times were not necessarily associated with a greater removal of carbon, but were more often due to some irregularity in the melting process or defect in the furnace. Fig. 2 shows the susceptibility in relation to the percentage of carbon eliminated in the "boil." When this was more than 0·5 per cent. the susceptibility was little affected, but when it was less than 0·5 per cent. the susceptibility tended to be greater as the elimination of carbon was less. Prolongation of the refining time in every case led to an increase in susceptibility to flaking as shown in Fig. 3. During refining, gas from the newly formed slag and the added ferro-silicon, is absorbed and practically no de-gassing of the metal occurs. Fig. 4 combines the data given in Figs. 1 and 3.

In the same steels, Myrzymow investigated the

effect of similar variations in melting procedure on the amount of non-metallic inclusions present in the steel. The results of his study indicated that to produce a steel as free as possible from non-metallic inclusions a limited duration both of the "boil" and the refining stage were necessary. The data are set out in a series of nine curves which also exhibit the effect of carbon, silicon, manganese, and chromium content. The main conclusion, as it affects the question of flakes in steel, is, however, that melting procedure, designed to diminish susceptibility to flake formation, will simultaneously tend to the reduction of non-metallic inclusions, or, at least, does not threaten to increase them in amount.

The results of Myrzymow's work confirm the supposition that there must be an important relation between susceptibility to flake formation and steel melting procedure. They indicate that to de-gas the melt a certain minimum amount of carbon must be eliminated during the boil and further that the refining time should be as short as possible. These conditions, as well as the avoidance of the introduction of materials containing hydrogen, are recommended as desirable in the melting of all kinds of steels which show a tendency to flake formation.



FIGS. 1–4.—*Data on the Influence of Melting Procedure on Susceptibility to Flake Formation in Ball-bearing Steel. (A. F. Myrzymow). The numbers at the points refer to the number of melts tested.*

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[1] *Metallurg*, 1937, 12, 21.
[2] *Metallurg*, 1937, 12, 70.
[3] *Metallurg*, 1938, 13, 39.
These papers are summarised in *Stahl und Eisen*, 1938, 58, 631, and 761.

The Action of Hydrogen on the Carbides of Iron and Chromium.

IN his investigations on the alteration of steel by hot hydrogen under pressure, L. Jacqué has put forward an explanation of the mechanism of hydrogen attack involving, first, the decarburisation of the steel as the hydrogen penetrates it, assisted by more or less accentuated intercrystalline cracking, and, secondly, the diffusion of the carbon from the still unaltered parts to those that have undergone change. Steels containing 3 to 6 per cent. of chromium, 0·5 per cent. of molybdenum, no nickel, and very little carbon were found to be unattacked, and this immunity was attributed to the combination of the carbon with the chromium to form chromium carbide which was assumed to be unattacked by hydrogen.[1]

In a recent paper, L. Jacqué[2] has produced evidence of the relative stability of iron and chromium carbides to attack by hydrogen. Iron carbide (Fe_3C) was produced by a method due to G. Charpy,[3] in which pure iron is acted on by fused potassium or sodium cyanide at 650 deg. Cent. The product was found to contain the theoretical amount of carbon for Fe_3C, viz., 6·67 per cent. The carbides of chromium were also produced synthetically by the action of pure carbon on electrolytic chromium at high temperatures.[4] Two products were made, one corresponding exactly to Cr_3C_2 and the other with a composition between Cr_5C_2 and Cr_7C_3.

By heating the carbide, Fe_3C, in a current of hydrogen at 425 deg. Cent. for several hours, Pengault found no loss of carbon, but by heating for 50 hours at 550 deg. Cent. in a slow current of hydrogen at atmospheric pressure Jacqué found that the carbon content was lowered to 6·25 per cent. A slightly greater decarburisation occurred in 20 hours at 600 deg. Cent. At high pressure the reaction becomes much more rapid. In experiments carried out in an internally heated autoclave, the duration of treatment being 50 hours, the following results were obtained :—

At 500 deg. Cent. and 50 kilos. per square centimetre pressure the carbon was lowered to between 2·5 and 3·5 per cent.

At 550 deg. Cent. and 50 kilos. per square centimetre pressure it was lowered to between 1·6 and 2·3 per cent.

At 550 deg. Cent. and 100 kilos. per square centimetre pressure, the carbide was entirely decomposed, the residue no longer containing any appreciable amount of carbon.

On the other hand, the carbide of chromium, Cr_3C_2, heated either at 500 deg. or 550 deg. Cent., and under a pressure of either 50 kilos. or 100 kilos. per square centimetre, showed no detectable change. Analogous results were obtained with the other chromium carbide, which, after treatment for 50 hours at 550 deg. Cent. under 100 kilos. per square centimetre pressure, did not show any appreciable loss of carbon.

These experiments show the considerable influence of pressure on the rate of reduction of iron carbide, and illustrate the stability of the carbides of chromium to hot hydrogen under pressure, thus confirming the previously suggested explanation for the superiority of low-carbon high-chromium steels in their resistance to the influence of hydrogen at high temperatures under high pressures.

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[1] See THE METALLURGIST, April, 1937, page 22.
[2] *Comptes Rendus*, June 20th, 1938, 206, 1900.
[3] *Comptes Rendus*, 1903, 136, 1000.
[4] *Comptes Rendus*, 1936, 203, 1007.

The Effect of Iron on Magnesium.

By W. R. D. JONES, D.Sc.

IT can be stated quite generally that small amounts of iron are not harmful when added to non-ferrous alloys. In many cases the effect of iron either directly or indirectly is beneficial. Magnesium and its alloys are usually produced in ferrous containers, so that a knowledge of the effect of iron on the metal is useful. Owing to the fact that molten magnesium will not dissolve iron to any appreciable extent, it has not been possible to produce iron magnesium alloys by the ordinary methods. Attempts have been made to add iron to magnesium by reducing pure iron oxide *in situ*. Extruded rods covered with a dried paste of red iron oxide were melted in a steel crucible closed with a tightly fitting steel lid. Repeated attempts were made to produce an alloy with 3 per cent. iron, but little more than about 0·1 per cent. could be determined in the alloy. If no flux were used the alloy was full of inclusions and the melting loss was excessive. Many of the fluxes used, such as "Elrasel," decreased the iron content still further. One of the best fluxes for this particular purpose is a mixture of magnesium chloride with magnesium fluoride. Better results were obtained when the iron was added in the form of fine sawings of ingot iron encased in a thick-walled capsule of magnesium metal which was placed in the molten magnesium. To prevent the sawings from fritting together before the capsule was dissolved the iron was mixed with sawings of magnesium metal. A series of ingots containing small amounts of iron was prepared in this way and their mechanical properties determined. The methods of melting, heat treatment, rolling, and testing followed generally those described in the *Journal* of the Institute of Metals, Vol. LXII., No. 1, 1938. The ingots were rolled with great care to prevent cold work by light passes and frequent annealings. Ingots were cast 1½in. diameter, maintained at 450 deg. Cent. for one hour, and then rolled to ⅞in. diameter in a three-high Robertson mill. The bars were straight after the finishing pass, showing that no cold work had taken place.

The results of the tests are given in the Table.

Effect of Iron on the Mechanical Properties of Magnesium.

Iron, per cent.	Condition.	Limit of proportionality, tons/sq. in.	Proof stress,† tons/sq. in.	Ultimate stress, tons/sq. in.	Elongation on 2in., per cent.	Reduction of area, per cent.	Brinell hardness number.‡
0·03	As cast	0·6	—	7·4	7·0	5·4	32
0·09	As cast	1·4	1·5	9·0	8·6	5·4	34
0·12	As cast	—	—	9·9	9·8	8·3	37
0·14	*As cast	1·4	1·6	8·1	5·8	7·2	39
0·26	As cast	1·5	1·5	8·5	5·4	5·8	40
0·10	Cast and heat treated one hour at 450 deg. Cent. and slowly cooled	1·4	1·6	9·1	6·7	7·2	34
0·12	Ditto	1·4	1·8	8·3	6·2	8·0	37
0·14	Ditto	1·3	1·6	7·1	4·8	4·0	36
0·26	Ditto	1·5	1·6	7·6	4·6	5·3	38
0·09	Cast and heat treated one hour at 450 deg. Cent. and quenched	1·1	1·2	8·8	5·7	6·1	38
0·11	§Ditto	1·1	1·2	6·9	7·3	8·0	39
0·11	Ditto	1·1	1·2	7·9	7·3	8·0	39
0·09	Ditto and tempered two hours at 200 deg. Cent. and quenched	1·0	1·3	8·6	7·3	6·5	35
0·07	As forged under hammer	4·2	7·3	15·9	11·2	15·9	37
0·10	As rolled	3·0	7·3	13·9	7·2	7·6	39
0·10	‖Ditto	3·0	7·3	10·9	0·25	1·6	40
0·24	Ditto	3·0	5·8	13·2	7·3	7·1	39
0·24	‖Ditto	2·6	5·0	13·5	1·2	2·8	42
0·07	Forged and heat treated one hour at 450 deg. Cent., slowly cooled	4·5	6·3	15·1	6·8	7·0	36
0·10	As rolled and heat treated at 450 deg. Cent. and slowly cooled	3·2	6·4	13·3	6·9	6·9	37
0·24	Ditto	3·9	5·6	13·2	7·8	7·9	38

* Casting temperature too low. † Permanent extension of not more than 0·025 per cent. of the gauge length of 2·0in.
‡ 500/10/30 secs. § Dirty metal. ‖ Cold worked or too severe reduction in the rolls.

In the cast state the mechanical properties are improved somewhat by small amounts of iron, but with more than about 0·14 per cent. the values are diminished. Iron decreases the values for the mechanical properties of rolled bars of magnesium. Some results in the table show that poor melting conditions and careless rolling conditions will easily decrease the values found for the mechanical properties to values lower than those due to the addition of iron.

Practically nothing is known concerning the constitution of the iron-magnesium alloys owing to the difficulty of producing the alloys. It is interesting to note that with an iron content as low as 0·10 per cent. a globular type of constituent can be observed when the alloy is examined under the microscope. This constituent forms a eutectic which is readily divorced on heat treatment and/or forging of the ingots, and bears no relation to the grain size. This constituent is probably a magnesium-rich compound of iron and magnesium.

In conclusion it can be stated that the effect of small amounts of iron on magnesium is not disadvantageous. Iron does not decrease the mechanical properties until present to an amount definitely much in excess of that which magnesium or its alloys can pick up during normal melting operations. Experiments were carried out some years ago to determine the iron pick-up by magnesium when melted in a new iron crucible. These experiments showed that the iron content of magnesium, or of copper-magnesium alloys, only increased from 0·08 to 0·15 per cent. after the molten material had been allowed to soak for a time very much longer than that which could be considered reasonable. A thin skin of magnesium or a magnesium-rich iron alloy is formed on the interior surface of the container and prevents iron from the apparatus entering the metal. With some of the recently developed fluxes such as "Elrasel" there is no iron pick-up, the iron content of the alloys produced being in many cases less than that of the ingot metal.

Cast High-Chromium Manganese Steels.

THE wide interest taken in the chromium-manganese alloys, arising from the possibility of replacing nickel in the nickel-chromium rust and scale-resisting steels by the cheaper element manganese, is reflected in the large number of papers which have recently appeared describing their structure and properties. Several of these, dealing with steels containing less than 20 per cent. of chromium, have formed the subject of review-abstracts in THE METALLURGIST.[1] Information about another group of these steels is contained in a paper by R. Kluke[2] on "The Influence of Manganese up to 20 per cent. on the Structure and Properties of Cast Alloys with 30 per cent. of Chromium." This paper contains a study of the structure, with special reference to the occurrence of the compound FeCr, of alloys containing 0·35, 0·6, or 1 per cent. of carbon with 0·5 to 20 per cent. of manganese and about 30 per cent. of chromium after various heat treatments. The mechanical properties of the alloys were determined at room temperature and at 500 deg. to 900 deg. Cent., the creep strength at 600 deg. to 1000 deg. Cent., and the resistance to scaling at 800 deg. to 1200 deg. Cent. The alloys were made from iron, ferro-chromium, and manganese metal in a basic arc furnace of 5 kilos. capacity and were cast into ingots 200 mm. long and 20 mm. diameter, which were allowed to cool in their sand moulds. A careful preliminary study was given to the structure as this provides a key to the subsequently described changes in properties.

The structure of the cast 1 per cent. carbon, 30 per cent. chromium alloy consists of a network of finely divided carbide in a gound mass of chromiferous ferrite. The addition of manganese up to 10 per cent. produced no essential difference when the carbon was below 1 per cent. The alloys were all strongly magnetic. A new constituent, identified as FeCr, appeared in alloys with 15 per cent. manganese and 0·35 per cent. carbon, and with 13 (or to a less extent 10) per cent. of manganese and 1 per cent. of carbon, accompanied by increased hardness. These specimens were workable only with difficulty and were weakly magnetic. The compound occurred in specks in the ground mass of chromiferous ferrite; the carbide network was undisturbed, and passed through ferrite or compound indiscriminately. In the high-carbon alloys the amount of compound present varied considerably in different positions in the ingot, an effect probably connected with the different rates of cooling of the different parts.

In all specimens with 20 per cent. manganese (or 15 per cent. and over when the carbon was 1 per cent.) the ground mass was wholly composed of FeCr, with a network of duplex structure probably containing chromium carbide, the alloys were extremely hard and brittle and were non-magnetic.

The cast specimens were annealed at 600 deg. to 1000 deg. Cent. for 100 hours and slowly cooled. The structure of the alloys containing up to 13 per cent. of manganese was unchanged, except for coalescence of the carbide; no precipitation of FeCr occurred. In specimens containing α+FeCr, and even in the 20 per cent. manganese alloys, no increase in the amount of FeCr was observed. The change above 900 deg. Cent. was not revealed by this annealing treatment as any FeCr transformed above 900 deg. Cent. was re-formed during slow cooling. In specimens containing up to 13 per cent. of manganese the structure was unaltered by quenching from temperatures between 700 and 1200 deg. Cent. The arrangement of chromiferous ferrite and carbide remained unchanged, and there was no noticeable solution of carbide. In specimens containing FeCr as ground mass, the compound remained unchanged up to 900 deg. Cent. Above 900 deg. it began to decompose, ferrite separated and with rise of temperature the decomposition proceeded further until at 1200 deg. Cent. it was almost complete. Given sufficient time it would probably be complete at 1000 deg. Cent., though the author states that it is impossible to determine the upper limit of the stable region of FeCr by quenching experiments alone, but that determinations of arrest points are required. Alloys containing α+FeCr showed decomposition of FeCr above 900 deg. Cent. with increase in the amount of ferrite, but on reheating below this temperature the amount of FeCr increased. The proportion of FeCr and ferrite also varied according to the rate of cooling from 1200 deg. Cent. The 20 per cent. manganese alloys after air cooling showed small specks of ferrite in the FeCr ground mass, while alloys with upwards of 10 per cent. of manganese showed an increasing amount of FeCr in the structure after very slow cooling. With 1 per cent. of carbon and over 13 per cent. of manganese the structure

of the slowly cooled alloy consisted of only FeCr and carbide.

On the basis of these observations the structure of the cast alloys with 0·6 to 1·0 per cent. of carbon and 30 per cent. chromium is summarised by the author as follows :—

Manganese content.	Structure.
(1) 0 to 10 per cent.	Ferrite and carbide
(2) 10 to 15 „ ...	Ferrite and carbide with FeCr
(3) Over 15 „ ...	The compound FeCr with carbide
(Or with higher carbon, 13 per cent.)	

Alloys of group (1) are technically serviceable and scarcely differ in structure and workability from cast 30 per cent. chromium steel. Group (2) consists of a

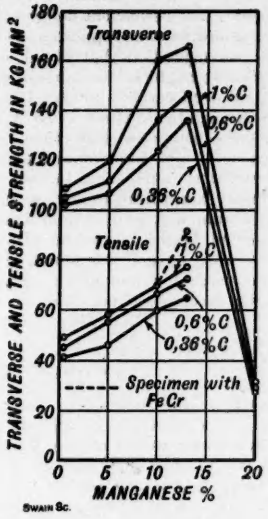
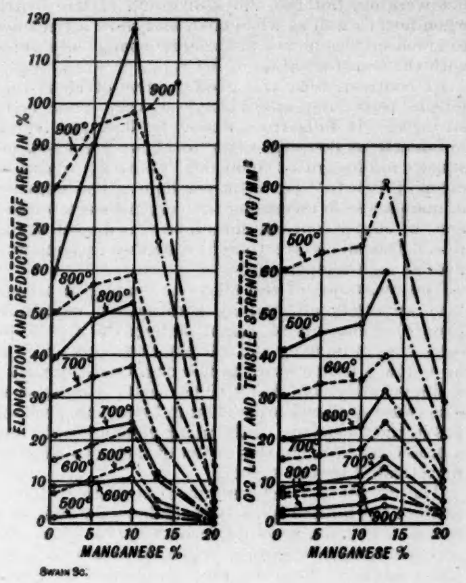


FIG. 1.—*Influence of Manganese and Carbon on the Strength of 30 per cent. Chromium Steel (Transverse Strength Measured on Bars of 10 mm. diameter and 160 mm. Between Supports).*

transition range of alloys (corresponding to the 38 to 44 per cent. chromium-iron alloys), the increasing brittleness of which with increase in manganese content renders them unsuitable for practical use. The alloys of group (3) are hard and extremely brittle.

At this point it may be worth comment that although the author refers continually to "the compound FeCr," it would be more accurate to refer to the phase as a solid solution (the Σ phase of Jette and Foote), and such a description would be consistent with the precipitation of ferrite which occurs "in the ground mass of FeCr," and the variable composition which the FeCr phase is shown to possess, including wide variations of manganese content.[3]

The tensile properties of the 30 per cent. chromium alloy at atmospheric temperature, and also at raised temperatures are improved by the addition of manganese up to a content of 13 per cent. (Figs. 1 to 3). With higher manganese the presence of FeCr makes the alloys hard and brittle. It is noteworthy that at high temperatures the elongation and reduction of area of the alloys of group (1) reach a high figure, which suggests the possibility of successful



FIGS. 2 and 3.—*Influence of Manganese on the Tensile Strength, Proof Load (0·2 per cent. Permanent Set), Elongation and Reduction of area of Cast 1 per cent. Carbon, 30 per cent. Chromium Steel at High Temperatures.*

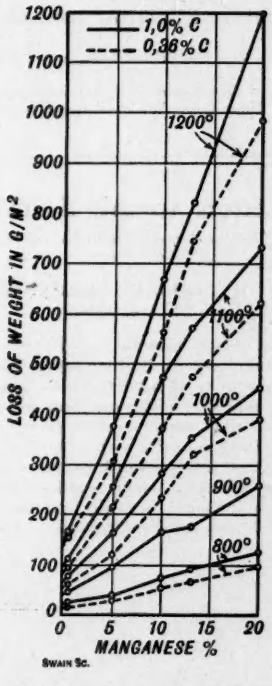


FIG. 4.—*Loss of Weight of Cast Chromium-Manganese Alloys with 30 per cent. of Chromium during 100 hours Annealing in Air.*

hot working, but the alloys of group (2) are brittle when hot, as well as when cold, and show a tendency to crack on account of the volume change associated with the transformation of FeCr.

In contrast with the good results of short-time tensile tests, the alloys have a very poor creep strength. It falls from about 4 kilos. per square millimetre at 600 deg. Cent. to about 0·2 kilos. per square millimetre at 1000 deg. Cent. for a rate of creep of 10×10^{-4} per cent. per hour. The influence of manganese in increasing the very poor creep resistance of 30 per cent. chromium steel is almost negligible. The alloys are therefore useless to support a load at high temperatures.

The resistance of the alloys to scaling in air was very adversely affected by additions of manganese (Fig. 4). The loss of weight suffered by the 30 per cent. chromium alloy at 1200 deg. Cent. was exceeded at as low a temperature as 900 deg. Cent. by that of a similar alloy containing 10 per cent. of manganese. The cause of this deterioration in behaviour probably lies in the incapacity of the manganese alloys to form a protective film, but this aspect of the matter was not investigated by the author.

The 30 per cent. chromium steel castings have a definite but limited sphere of usefulness for annealing-boxes, lead pots, roasting furnace rabble arms, &c., and additions of silicon, nitrogen, or nickel are sometimes made to improve their properties in various respects; but the work of Kluke, here described, appears to indicate that the addition of manganese to 30 per cent. chromium steel is in all cases injurious, since the most important properties of this corrosion and heat-resisting alloy are thereby likely to be lost.

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[1] THE METALLURGIST, February, 1937, page 11; April, 1938, page 123.

[2] *Archiv für das Eisenhüttenwesen*, June, 1938, 1937/38, 11, 615.

[3] See also "Constitution of Iron-Chromium-Manganese Alloys," C. O. Burgess and W. D. Forgeng, *Metals Technology*, 1938, 5, (3),

Letters to the Editor.

(We do not hold ourselves responsible for the opinions of our correspondents.)

CRACKING OF STEEL IN AMMONIUM NITRATE SOLUTIONS.

SIR,—I was greatly interested in your article on nitrate cracking of mild steels in the June issue. Some years ago I had the opportunity of examining metallurgically a large number of samples of mild steel plant which had failed in this manner while handling solutions of nitrates. Two significant features were observed. First, failures were confined to mild steel plant in which calcium and ammonium nitrates were handled; plant handling sodium nitrate appeared to be immune. Secondly, microscopic examination suggested that the intercrystalline attack was connected with chemical attack on the iron carbide in the steel, when located in or contiguous to the crystal boundaries. Now, in most low-carbon mild steel, even in the normalised condition, a certain amount of cementite is distributed in the crystal boundaries, either in globules or thin films, and it did not appear unreasonable that intercrystalline attack should be the result of selective decomposition of this cementite, the resultant expansion due to the formation of corrosion products further opening the boundaries and allowing attack to continue in the body of the steel. It was finally observed that only those liquors containing ammonium nitrate, *i.e.*, calcium nitrate containing some ammonium nitrate, and ammonium nitrate itself, caused disintegration to occur. Where a nitrate liquor was free from ammonium nitrate, *e.g.*, the sodium nitrate solution referred to, no trouble was experienced, according to plant records, even in riveted joints. Further, Jones's statement, that permanent deformation must first have occurred, appeared to be supported in all cases.

To confirm the suggestion that attack of ammonium nitrate on cementite might be the cause of disintegration, a sample of pure iron carbide, prepared electrolytically, was obtained through the kindness of Dr. W. H. Hatfield, and its behaviour in contact with chemically pure solutions of sodium, calcium, and ammonium nitrates examined. The results were very interesting, in that no attack on carbide was found except from ammonium nitrate. In the case of the calcium and sodium solutions, the carbide particles remained bright in neutral atmospheres, but rusted slightly when oxygen was admitted to the apparatus. In the case of ammonium nitrate, the carbide appeared to be decomposed according to the following reaction:—

$$15\ H_2O + 3\ NH_4NO_3 + 4\ Fe_3C \longrightarrow 12\ Fe(OH)_2 + 6\ NH_3 + 4\ C.$$

The ferrous hydroxide oxidised to ferric when oxygen was admitted to the apparatus. Sufficient ammonia was collected from a known weight of pure ammonium nitrate to show that the nitrate radicle, as well as the ammonia radicle, was being decomposed, but the reaction could not be completed owing to accumulation of hydroxide which coated the remaining particles of carbide. However, some undecomposed ammonia was later distilled off the solution with caustic soda, showing that, though nitrate nitrogen had been evolved, some undecomposed ammonium nitrate still remained.

It had been intended to carry out a complete investigation on the lines suggested by these results, but for various reasons this had to be abandoned. As your contributor points out, the cause of the nitrate cracking phenomena has never been finally established, and the parallel case of caustic embrittlement occurs in such different solutions that the same effective agent is unlikely to be responsible in each case. Perhaps the foregoing observations may suggest an alternative line of investigation to those interested in the problem.

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